SRNL
SAVANNAH RIVER NATIONAL LABORATORY
Operated by Savannah River Nuclear Solutions, LLC
We Put Science To Work

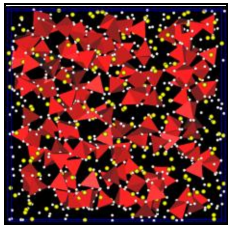
OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

# Hanford Low Activity Waste (LAW) Fluidized Bed Steam Reformer (FBSR) Na-Al-Si (NAS) Waste Form Qualification


C.M. Jantzen and E.M. Pierce


November 18, 2010






EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

# Participating Organizations

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

Pacific Northwest
NATIONAL LABORATORY

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

THOR Treatment Technologies LLC

BERKELEY LAB

UC DAVIS
UNIVERSITY OF CALIFORNIA

washington river protection solutions

SRNL

EM Office of Environmental Management
safety ✧ performance ✧ cleanup ✧ closure

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

# Incentive and Objectives

**FBSR sodium-aluminosilicate (NAS) waste form has been identified as a promising supplemental treatment technology for Hanford LAW**

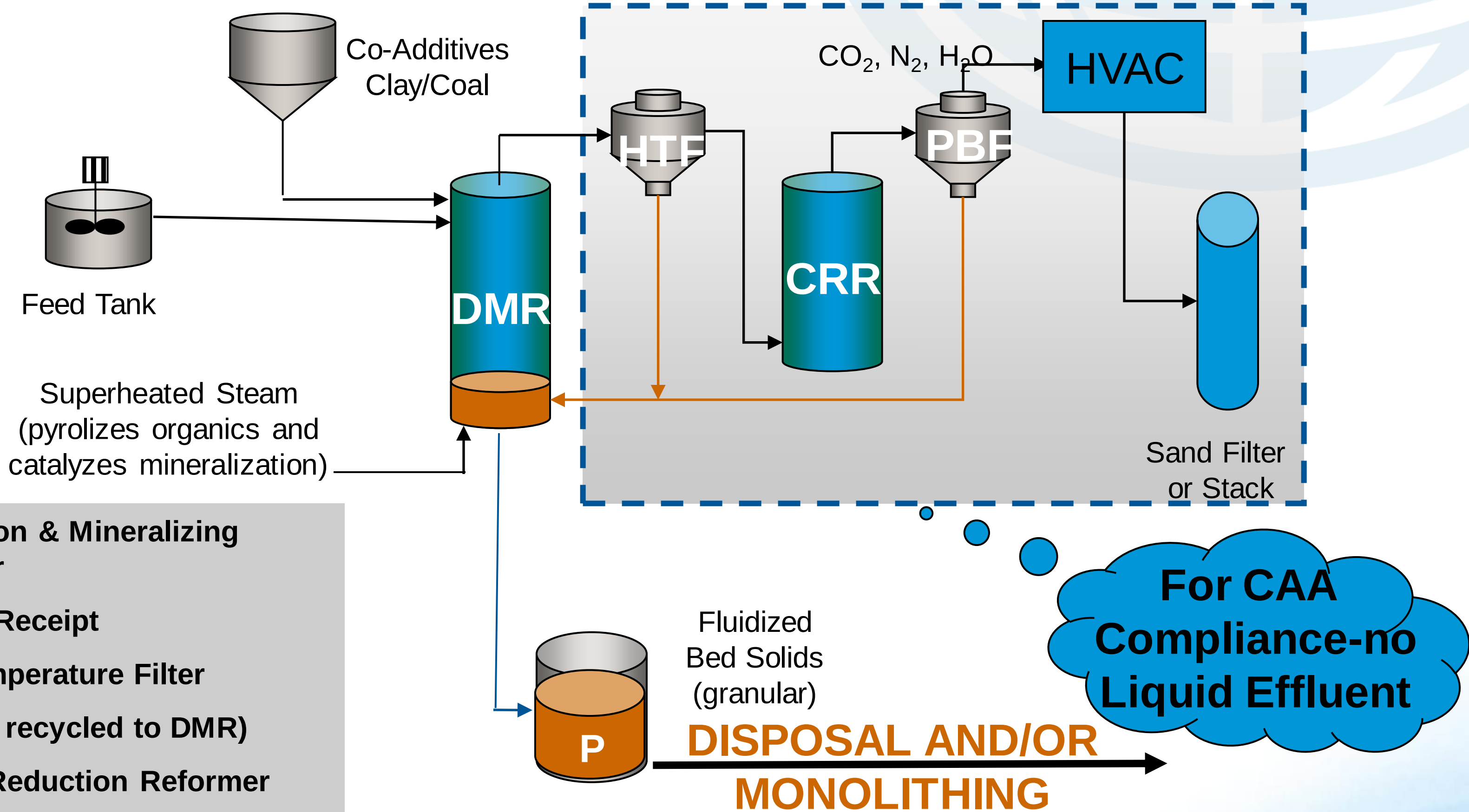
## Objectives:

- **Reduce the risk associated with implementing the FBSR NAS waste form as a supplemental treatment technology for Hanford LAW**
  - Conduct test with actual tank wastes
  - Use the best science to fill key data gaps
  - Linking previous and new results together

# Outline

- FBSR NAS waste form processing scales
- FBSR NAS waste form data/key assumptions
- FBSR NAS key data gaps
- FBSR NAS testing program

# FBSR NAS Waste Form Processing




| | |
|---|---|
| **DMR =** | **Denitration & Mineralizing Reformer** |
| **PR =** | **Product Receipt** |
| **HTF =** | **High Temperature Filter** |
| | **(material recycled to DMR)** |
| **CRR =** | **Carbon Reduction Reformer** |
| | **(treats gases only)** |
| **PBF =** | **Process Bag-house Filter** |

# FBSR NAS Waste Form Processing Scales

8-Years of Engineering Scale Test Demonstration (ESTD) with simulated waste

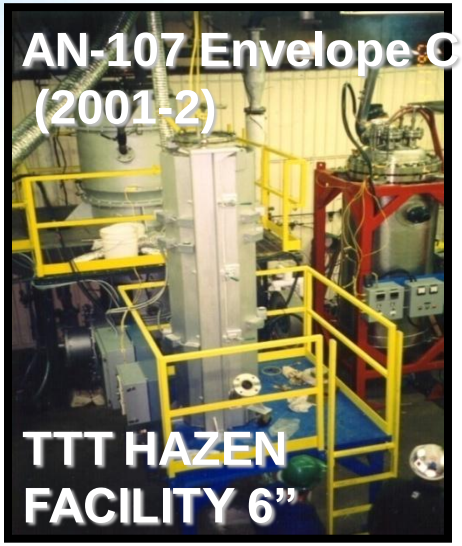
- Hazen 2001 (auto-catalytically heated 6”)
- Hazen 2006 and 2008 (auto-catalytically heated 15”)
- SAIC-STAR Test Facility 2003-4 (externally heated 6”)

Bench-Scale Steam Reformer (BSR)

- Designed and built at SRNL in 2004
- INL SBW simulant tested
- Hanford Envelope A composite (68 tank) simulant tested
- Redesigned for Shielded Cell Facility (SCF) in 2006

# FBSR NAS Waste Form Processing Scales: From Engineering Scale Pilot to Bench-Scale

NON-RADIOACTIVE






NON-RADIOACTIVE
+ RADIOACTIVE



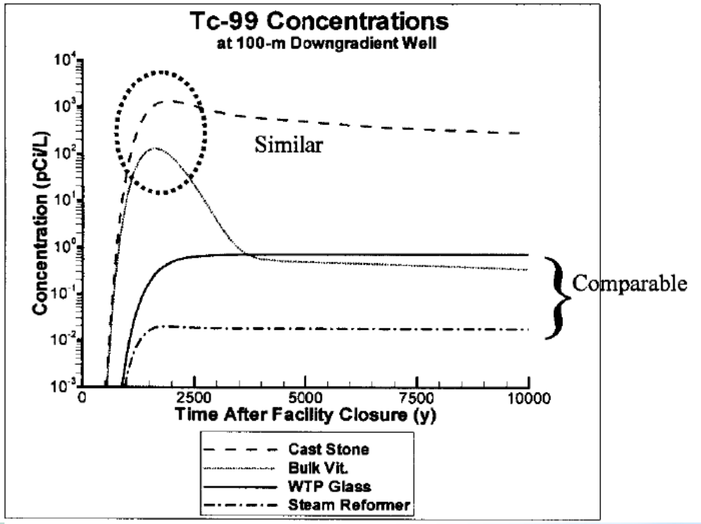
# Wastes Processed and Tested at Pilot Scale and BSR

## Simulated wastes tested (all doped with Re for Tc)

- Hanford Envelope C Tank Waste (AN-107)
- Hanford Envelope A (68 tank blend) Tank Waste
- Hanford WTP secondary waste
- INL sodium bearing waste

## Testing Performed:

- Product Consistency Test (PCT; ASTM C1285)
  - on bed product (with and without coal removed)
  - on fines (with and without coal removed)
  - Potential Al-buffering mechanism identified
- Single Pass Flow Through (SPFT; ASTM C1662)
  - on bed product (with coal removed)
- Pressure Unsaturated Flow (PUF) test
  - on bed product (with coal removed)
- Preliminary Performance Assessment (PA) performed



# FBSR NAS Waste Form Data/Key Assumptions: Distribution of Minerals

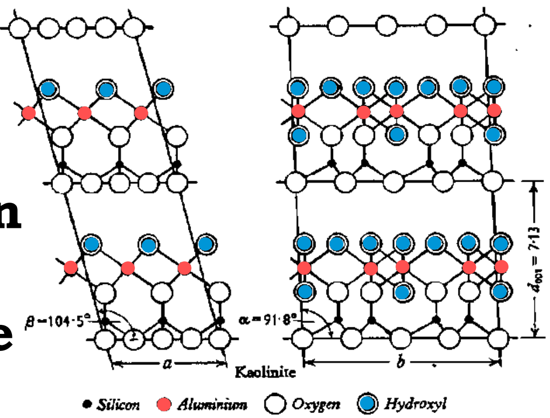
## Why important: impacts contaminant release

- Multi-phase waste form – Nepheline, Sodalite, & Nosean
- Nepheline – dominant mineral
  - Dissolution may affect other minerals
- Sodalite & Nosean - minor phases dependent on anion content of waste
  - Both are 6 unit cells of nepheline in a configuration that creates a cage
- Sodalite expected to contain COCs
- Anion content may compete with Tc for “cage” sites

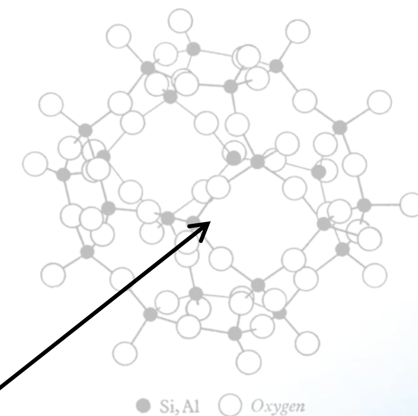
<u>Theoretical Calculation</u>:

| | |
|---|---|
| accommodates 7.9 wt% Cl | - (Cl/Na ratio = 0.25) |
| accommodates 28.3 wt% I | - (I/Na ratio = 0.25) |
| accommodates 4.2 wt% F | - (F/Na ratio = 0.25) |
| accommodates 10.8 wt% $SO_4^-$ | $^-$ ($SO_4$/Na ratio = 0.25) |
| accommodates 40.7 wt% Re | - (Re/Na ratio = 0.25) |
| accommodates 21.7 wt% Tc | - (Tc/Na ratio = 0.25) |

Kaolin
+
Waste




Sodalite

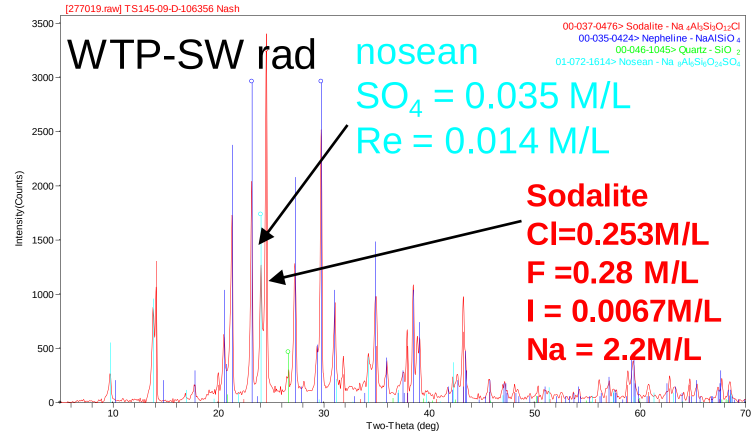


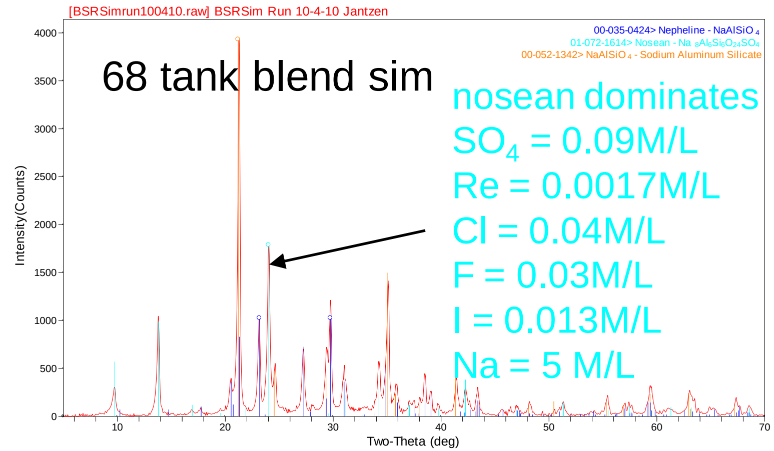

Cage

# FBSR NAS Waste Form Data/Key Assumptions

**Joint SRNL/INL/TTT/SAIC-STAR Testing**

- **SRNL developed process control strategy (MINCALC™) to estimate mole % or wt% of each phase in the FBSR product**
  - **sodalite family of minerals have cage structures that accommodate Cl, F, I, $SO_4$ or S, B, Mo, Re, Tc, Be, Zn, Mn, P**
    - **sodalites known to sequester these species in other HLW waste forms (glass bonded sodalites and supercalcine ceramics)**
    - **Re sodalite made phase pure by Mattigod at PNNL and structure determined**
    - **known from XRD patterns of simulants containing high Cl and F (WTP-SW) produce sodalite; high $SO_4$ simulants produce nosean (sodalite analog with sulfate)**




SRNL

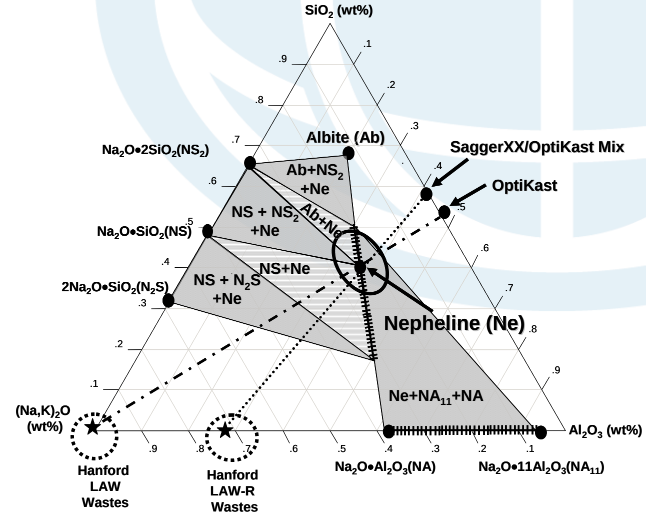
EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

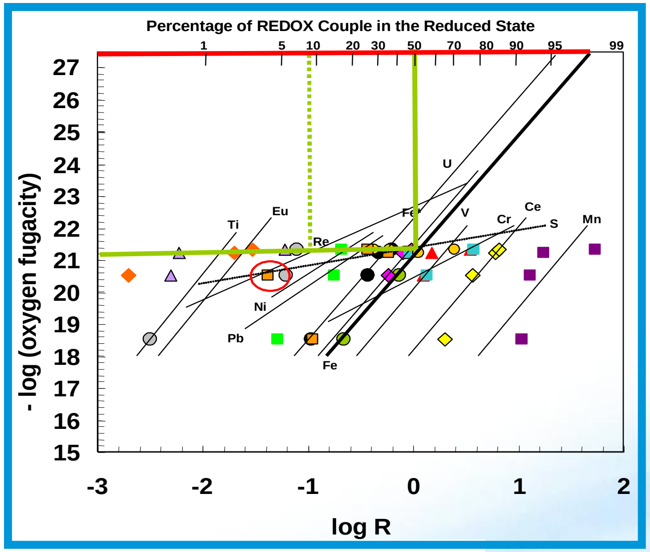
OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

# FBSR NAS Waste Form Data/Key Assumptions

**Joint SRNL/INL/TTT/SAIC-STAR Testing**

- SRNL developed process control strategy (MINCALC™) to accomodate high $Al_2O_3$ or high Na and anion containing wastes
- Off-gas testing at Erwin (commercial facility) and SAIC STAR and ESTD Hazen and product testing at SRNL indicates:
  - dual reformer flowsheet minimizes volatilization of species (Cs,Re,I - see next slide)
    - CAA and MACT-HWC compliant
- Re speciation monitored by development of an Electromotive Force (EMF) series and REDuction/OXidation (REDOX) control
  - forces Re to oxyanion $Re^{+7}O_4^-$ which forces it into sodalite/nosean cage structure
  - forces S to oxyanion $SO_4^{-2}$ into nosean cage structure but cage can accommodate $S^{-2}$ as well.



# Off-gas vs. Product Retention

| Element | Product Retention (%) | |
|---|---|---|
| | 2001 (Hazen 6" Scoping Test ~5 hrs) | 2008* (Hazen 15" Dual Reformer) |
| Cs | 99.90 | 99.99 |
| Re | 99.997 | 99.99 |
| Cl | 96.6 | 86.4-95.1 |
| F | >96.0 | 83.4-85.8 |
| I | not added | 89.4-94.4 |

*Hanford mineralizing runs only

**Data from RPP-RPT-47063 (2010) as summarized from TTT's Reports**

**WSRC-TR-2002-00317 (July, 2002).**

# Summary of Key Assumptions

Redox conditions for BSR are consistent for non-radioactive and radioactive sample production

- Also must be reflective of ESTD pilot-scale conditions

Strategy for WFQ presumes Tc and I are contained in "cage"

No significant difference between mineral assemblages produced in the BSR system in comparison to pilot-scale FBSR system (verified on WTP-SW and SRS LAW)

Correlation between data obtained from nonradioactive simulants and actual radioactive samples

# Program Overview: Key Data Gaps – high level summary

**Processing Gap:**

- **ESTD pilot-scale tests and BSR tests conducted with simulants using**
  - **actual Hanford waste tests needed in BSR**
  - **SRS wastes trimmed to mimic Hanford WTP-SW and 68 tank blend (Envelope A) in BSR in progress**

**Contaminant release Gaps:**

- **Verify the % distribution of key minerals in FBSR NAS waste form predicted by MINCALC™ process control**
- **Technetium speciation and distribution amongst the mineral phases contained in the NAS waste form** **(continued on next slide)**

SRNL

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

# Program Overview: Key Data Gaps – high level summary

**Contaminant release Gaps (continued):**

- **Evaluate the impact, if any, of the monolithing (binder) process on material performance**
- **Determine the effect of chemical affinity on contaminant release for multi-phase material**
- **Develop rate law parameter and thermochemical data for the major mineral phases contained in FBSR NAS waste form**
- **Determine transport properties of monolith waste form – diffusion release**
- **Develop a modified waste form release/radionuclide source term model for the FBSR NAS waste form**

# Actual Waste Samples Selected

## Criteria:

- Obtain samples from existing 222-S archive
- Samples that range anion content (anions may compete for “cage” with Tc)
  - Evidence suggests anion content maybe linked to phase formation, which maybe a key control during processing
- Previously tested as part of LAW glass evaluation process
- Linkage to proposed early retrieval (retrieved in 5 – 7 years)
- Linkage to previous pilot-scale FBSR tests

## Samples selected

- 68 Tank Blend (SRS shim sample) “quick win”
  - Links material performance from BSR system to ESTD pilot-scale FBSR system
- Tank SX105 (high anion)
- Tank AN103 (low anion)
  - Provides link to previous LAW vitrification experiments

# Technetium Speciation

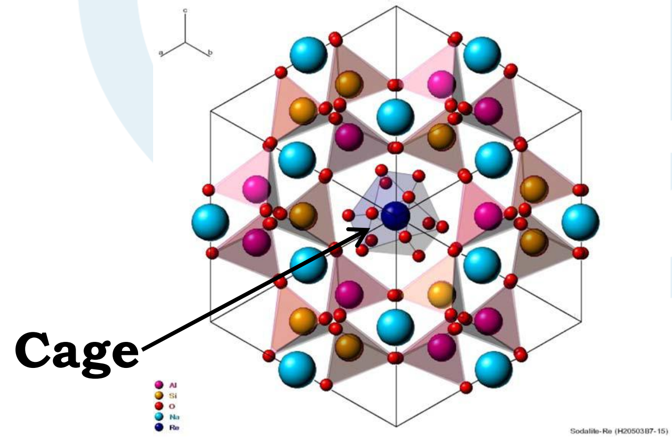
**Why important: impacts contaminant release**

- Tc(VII) – potentially incorporated in “cage” structure
- Tc(IV) –not incorporated in “cage” structure

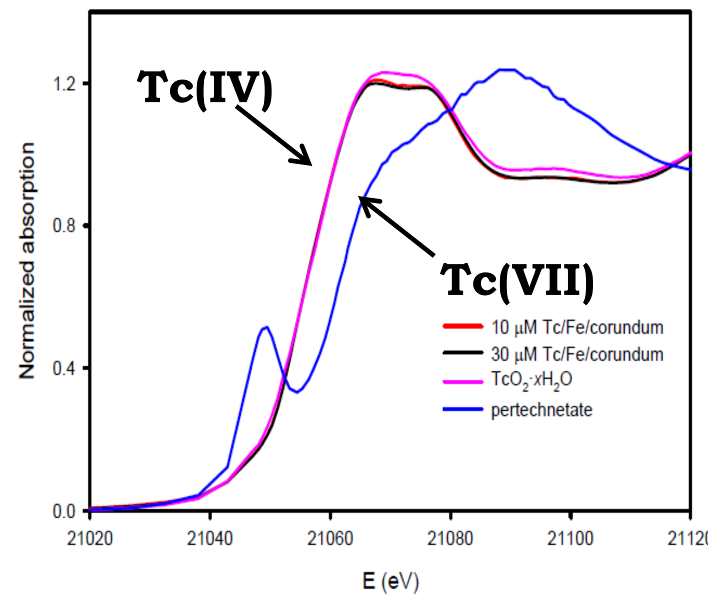
**Approach: X-ray absorption spectroscopy**

**Representative samples being analyzed for Re and/or Tc**

- Analysis at APS, NSLS, and/or SLAC
- Also attempting iodide (unclear it will be successful - performed less)




Re–sodalite



# Other Key Aspects

## Impact of Monolith Process

- Required to meet disposal regulations
- Curing process may alter mineral assemblage
- Dominant release mechanism may change – diffusion vs. dissolution vs. solubility or a combination (not seen in testing to date)
- Binder matrix may affect contaminant release

## "Pure" phase minerals

- Required for updated source term model
- Provides insight into the effect of one mineral on another

## Contaminant release mechanism (preliminary source term release)

- Release from granular/monolith material under relevant conditions

## Update source-term release model

- Required for full PA computer simulations

# Comparison of Rhenium and Technetium

Similar cation size in VII oxidation state

Similar oxyanion size in VII oxidation state

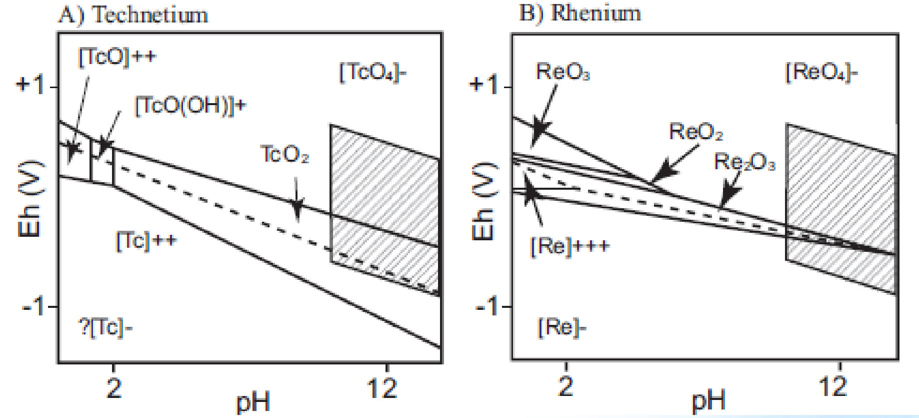
- 1.702 ($TcO_4^-$) and 1.719 ($ReO_4^-$)

Indication of differences in reduction and volatization

- Easier to reduce Tc in comparison to Re
  - Krupka et al. (2006). IHLRWM Conference
  - McKenown et al. (2007). ES&T

*Comparison of properties of Tc and Re*

| *M* = Tc or Re | Tc | Re |
|---|---|---|
| Principal oxidation states: | IV, VII | III, IV, VII |
| Cation (VII) size (pm) | 51[a] | 52[a] |
| Cation (IV) size (pm) | 78.5[a] | 77[a] |
| *M*(VII)—O Å | 1.702[f] | 1.719[j] |
| *M*(IV)—O Å | 1.98[b] | 2.00[i] |
| *M*(IV)—S Å | 2.33[e] | 2.36[c] |
| $E_{hyd}$ (eV) | -2.4[g] | -2.5[g] |
| Binding energy (eV) | -388.7[g] | -371.1[g] |
| $MO_2/MO_4^-$ (V) | -0.747[d] | -0.510[h] |




Icenhower et al. (2010). Amer. Jour. Sci. Vol. 310

SRNL

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

# Rate Law Model For Mineral/Glass Weathering

$$r = \vec{k}_o a_{H^+}^{\pm\breve{\eta}} \exp\left(-\frac{E_a}{RT}\right)\left(1-\frac{Q}{K(T)}\right)^{\sigma}$$

Rate constant

pH coef.

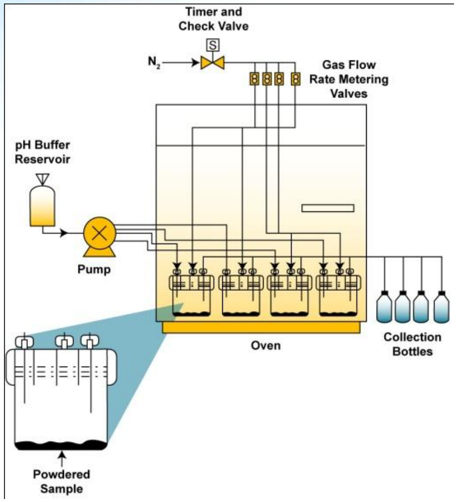
Activation Energy

Equilibrium Constant

Temkin Coefficient

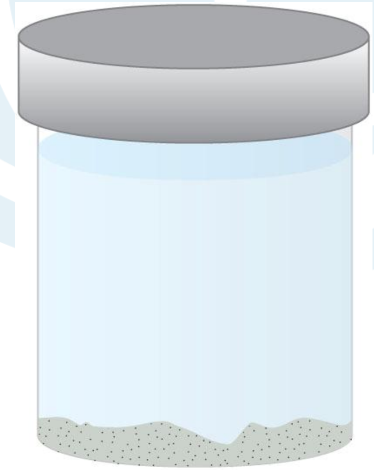
Based upon Transition State Theory

# Common Test Methods




Flow through test

PUF apparatus



PCT A/B

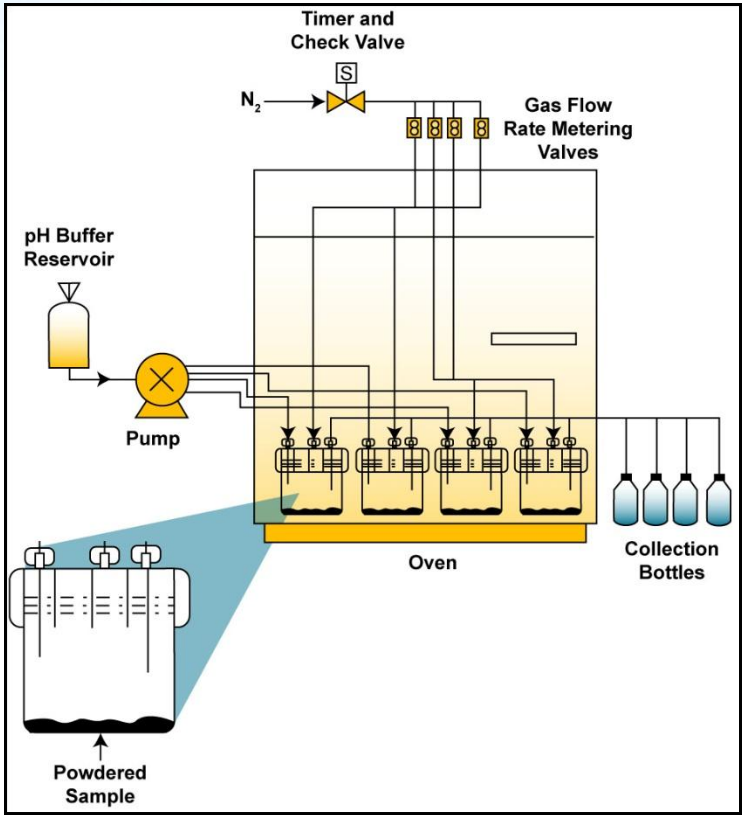
**PCT (B) – Long-term behavior under saturated conditions**

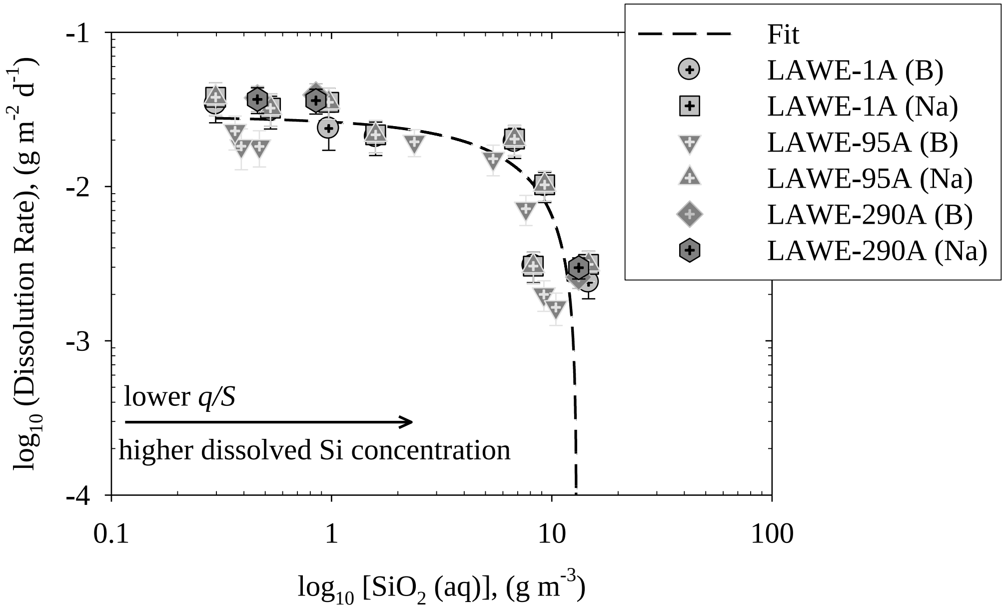
**SPFT – Determine parameters for fixed set of environmental conditions**

**PUF – Evaluates long-term glass behavior under disposal relevant conditions**

# Effect of Chemical Affinity on Dissolution

## *Single-Pass Flow Through Test*

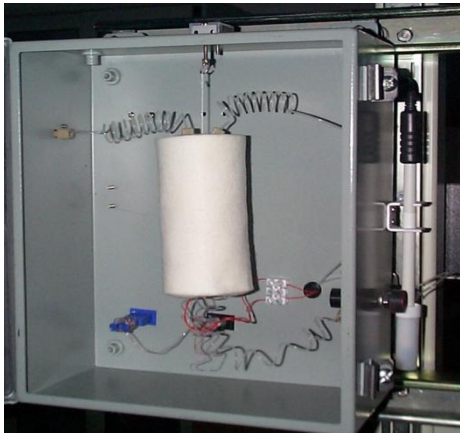


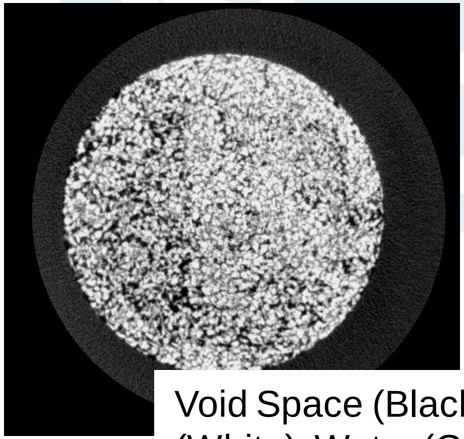




Pierce et al. (2008). Vol. 5(1): 73-85. Environmental Chemistry

SRNL
EM Office of Environmental Management
safety ✧ performance ✧ cleanup ✧ closure
OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

# Pressurized Unsaturated Flow Apparatus





XMT-CT Scan

Void Space (Black), Particles (White), Water (Grey)

**Accelerate "aging" of Waste Forms**

- Hydraulically Unsaturated
- Steady Volumetric Flow Rate
- Elevated Temperature

**Real-time monitoring**

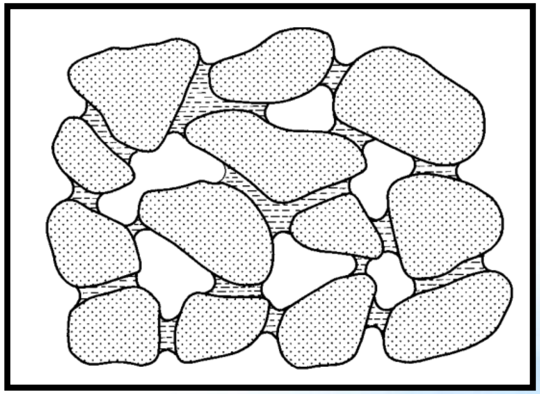
- Bulk Water Content
- Effluent Chemistry
- Real-time pH & EC

**Spatial Imaging via X-ray Micro-tomography**

**Computed Tomography**

Changes in Pore Structure

Moisture Distribution



SRNL

Office of Environmental Management

safety ✦ performance ✦ cleanup ✦ closure

Oak Ridge National Laboratory

Managed by UT-Battelle for the Department of Energy

# Status of Current Activities

WTP-SW BSR runs (sim and rad complete)

BSR 1st LAW sample (sim complete; rad in progress)

2 of 3 Hanford samples have been shipped and received by SRNL

Pilot-scale THOR Treatment Technologies (TTT) samples (in progress)

- Distribution of mineral – granular sample
- Monolith prepared – currently curing
- Sample of material shipped from SRNL to PNNL
- Treatment of granular sample planned to start next week
- 1st XAS analysis Nov.1 – 4 at NSLS (BNL) – Re speciation

White paper on performance data (in progress)

- Assembles existing data to support early decision

# Evaluation Points – Off Ramps

**Quarterly progress briefing to DOE-EM**

**Mass balance of Re, I, and Tc from SRS LAW shim sample**

**Tc speciation using the SRS LAW shim**

- **Combination of results from XAS, SEM-EDS, SPFT, etc.**

**Contaminant release**

- **Dissolution tests**
- **Monolith immersion tests**

# Available Data

In accordance with DOE Order 413.3 – critical decision process

CD-0 package (submitted to DOE HQ)

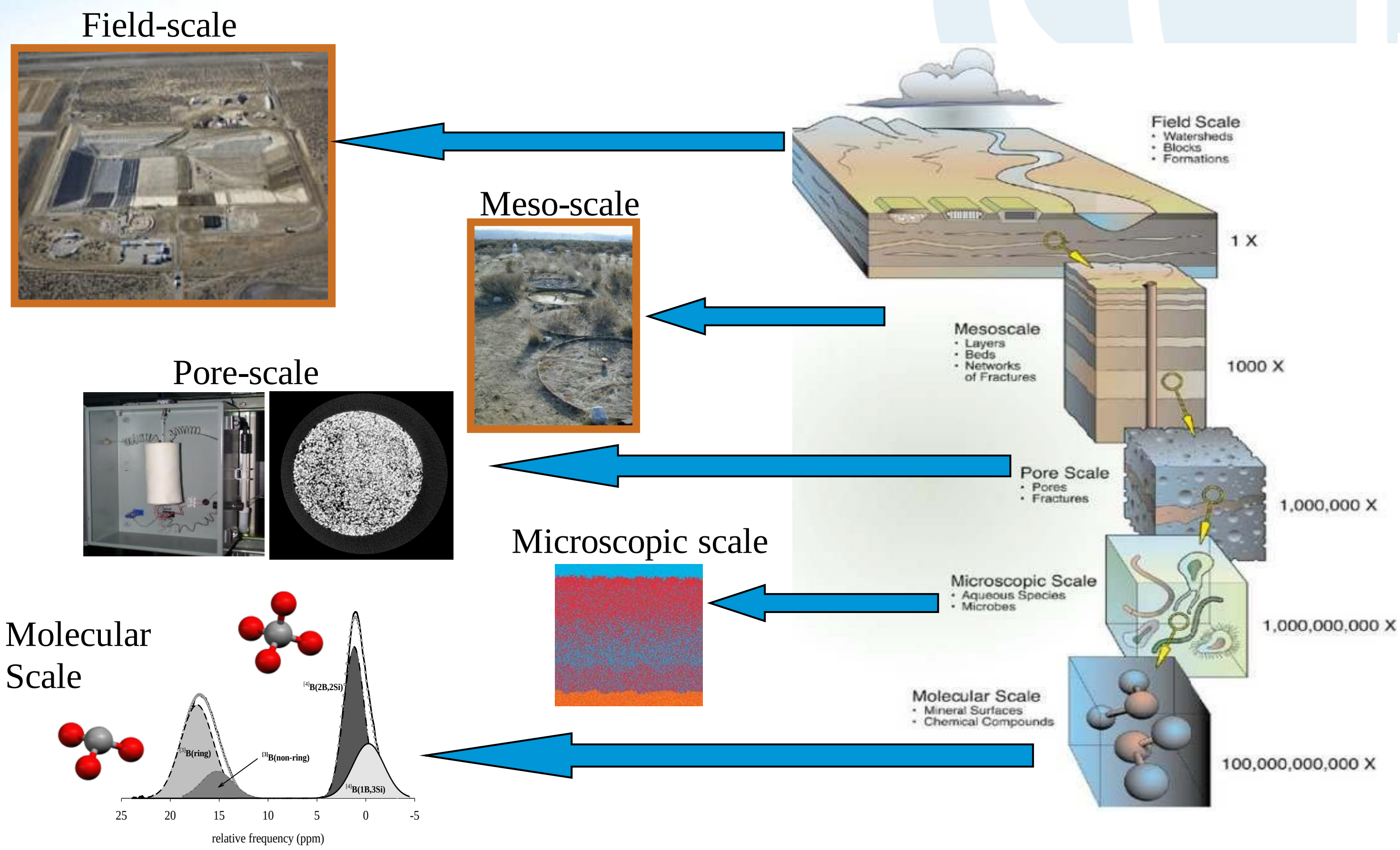
CD-1 package (high level summary)

- White paper discussing all existing data on FBSR product
- Evaluation of Tc and I incorporation in the FBSR product based on BSR material (mass balance)
- Evaluation of Re, Tc, and possibly I in the granular and monolith FBSR and BSR material for at least one radioactive LAW sample

CD – 2/3 (if selected)

- Update source term model that desribes the perfomance of the FBSR material

# Example of Length Scales – Questions?????




***Increase Temporal and Spatial Resolution to Explain Processes Across Scales.**
***Solid Technical Foundation for Predictions – Science to Solution**

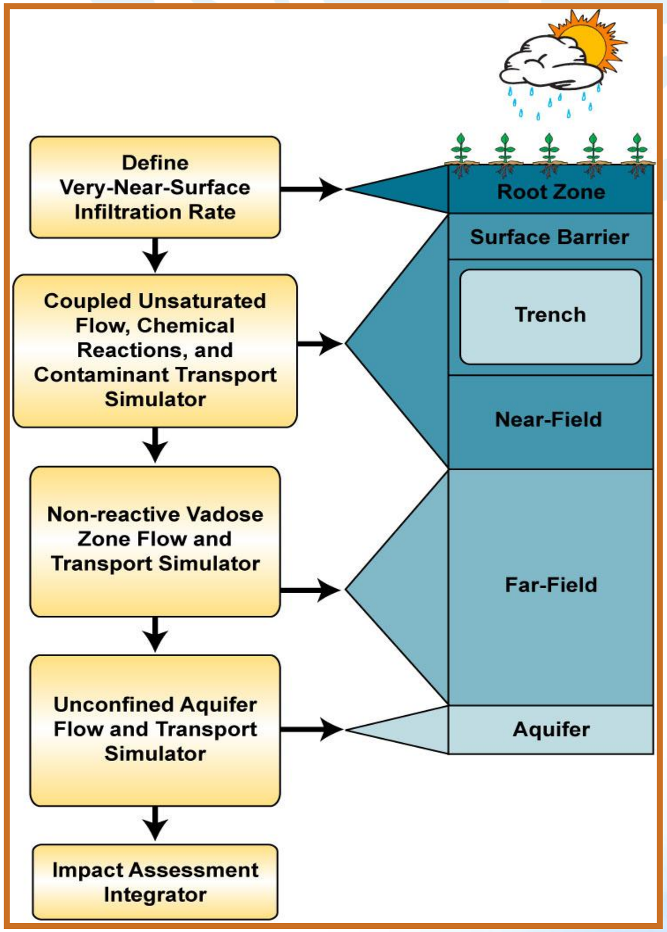
SRNL
EM Office of Environmental Management
safety ✦ performance ✦ cleanup ✦ closure
OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

# Backups

# Overview of Integrated Strategy

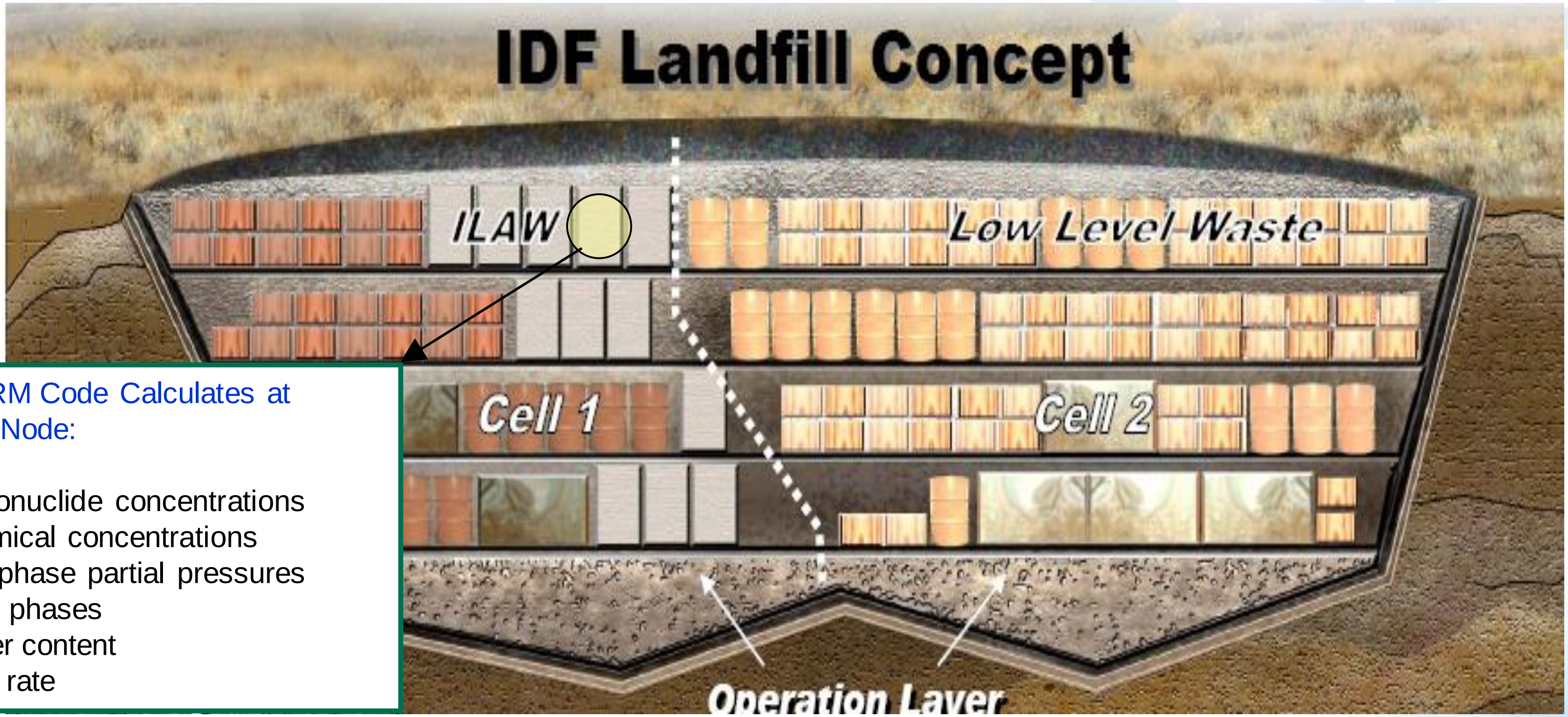
- Subsurface water and gas flow
- Waste glass dissolution
- Transport of aqueous and gaseous chemical species
- Kinetic and equilibrium chemical reactions
- Secondary mineral dissolution and precipitation
- Coupling between hydraulic properties and mineral precipitation and dissolution
- Model abstraction not used

Glass/FBSR is the major engineered barrier



# Integrated Strategy, cont.

- Full-coupled model – physical, chemical, and hydraulic processes




STORM Code Calculates at Each Node:
- pH
- Radionuclide concentrations
- Chemical concentrations
- Gas phase partial pressures
- Solid phases
- Water content
- Flow rate